STUDIES ON SHRINKAGE PHENOMENON. XII. EFFECT OF USING PROCESSING LIQUOR AS HEATING AND RECOVERY MEDIUM ON THE SHRINKAGE PROPERTIES OF COLLAGEN FIBRES

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The effect of using process liquor instead of water as heating and recovery medium on the shrinkage behaviour of collagen fibres subjected to pretanning treatments is assessed and compared to the shrinkage behaviour of skins under similar conditions. In contrast to the shrinkage behaviour of limed skin, wherein T_s and AS (Area shrinkage) is decreased and AR (Area recovery) is increased; in the case of limed collagen fibre, only T_s is decreased on using lime water instead of water as heating and recovery medium. This is attributed to the poor solubility of lime at higher temperature accompanied with less deposition of lime within the fibre bundle because of the absence of the three dimensional network. Similarly T_s and LS (Linear shrinkage) of pickled fibres are increased and LR (Linear recovery) decreased on using pickle liquor instead of water as heating and recovery medium. The results confirm that the absence of swelling forces when pickle liquor is used as the medium and the swelling of pickled fibres caused by limited dilution when water is used as the medium are responsible for the observed shrinkage behaviours of pickled samples.

The hydrothermal shrinkage behaviour (T_s and dimensional shrinkage properties) of skin and collagen fibre undergoing pretaining treatment was discussed in earlier papers.[1-3] Studies were also carried out with skins to find out the effect of diffusion of chemicals present in the pelt into water, the heating and recovery medium.[4] The shrinkage behaviour of skins and collagen fibres reported in the earlier paper[1-4] was also confirmed by statistical evaluation of results (unpublished data). When hydrothermal shrinkage of limed skins were measured in lime liquor instead of water, shrinkage temperature (T_s) and area shrinkage of limed samples were decreased and recovery increased. When, however, tests of pickled skin samples were made in pickle instead of in water, T_s and area shrinkage were increased and recovery decreased. Skins and collagen fibres do not always behave in similar manner towards shrinkage.[3] T_s and AS of limed skin samples in water were higher than that of raw or delimed skins, but the collagen fibre did not exhibit any difference in the shrinkage proper-

ties of raw, limed and delimed samples[3] in water. Area shrinkage can be considered to be the result of linear shrinkage in two planar directions. Hence a study of shrinkage behaviour of collagen fibres in process liquor i.e. using process liquor as heating and recovery medium instead of water, was considered essential for better understanding of the shrinkage phenomenon. For this purpose fresh RTT collagen fibres preserved in 0.5 M salt solution were subjected to pretanning treatment. The method of processing was reported in the previous paper.[4] At each stage of pretanning operation, T_s and dimensional shrinkage properties of adjacent small pieces of collagen fibre bundles were determined using the micro technique, also detailed in the previous paper, and the values were statistically analysed and compared. For statistical evaluation of the results fifty samples were tested at each stage of pretanning treatments. While discussing the results, changes in the diameter of the fibre bundles on shrinkage and changes in length and diameter on transferring the fibre from the process liquor into water for carrying out the shrinkage in water were also taken into account.

For presenting and discussing the results, the following abbreviations are used:

l_1 initial length of the fibre in the process liquor.

d_1 initial diameter of the fibre in the process liquor.

l_w initial length of the fibre in the heating medium (before shrinkage).

d_w initial diameter of the fibre in the heating medium (before shrinkage).

l_2 length of the shrunken fibre in the heating medium.

d_2 diameter of the shrunken fibre in the heating medium.

l_3 length of the recovered fibre in the recovery medium.

d_3 diameter of the recovered fibre in the recovery medium.

$dL\% = \frac{l_1 - l_w}{l_1} \times 100$ percent change in length on transferring the fibre from the process liquor into heating medium.

$dD\% = \frac{d_1 - d_w}{d_1} \times 100$ percent change in diameter in transferring the fibre from the process liquor into heating medium.

$LS\% = \frac{l_1 - l_2}{l_1} \times 100$ percent linear shrinkage.

$dS\% = \frac{d_1 - d_2}{d_1} \times 100$ percent increase in diameter due to shrinkage.

$LR\% = \frac{l_3 - l_2}{l_1 - l_2} \times 100$ percent linear recovery.

Results and discussion :

It is seen from table 1 that only shrinkage properties of limed and pickled collagen fibre samples were affected by the use of process liquor as heating medium instead of water. LS of pickled samples is increased and LR is decreased on using pickle as heating and recovery medium instead of water.

The lowering of T_s of limed collagen samples in lime water compared to that

Table 1

COMPARISON OF MICRO SHRINKAGE VALUES OF COLLAGEN FIBRE SUBJECTED TO PRETANNING TREATMENTS IN WATER AND RESPECTIVE PROCESS LIQUOR*

		Sampling stage		
	Raw	Limed	Delimed	Pickled
T_s°C	55(54)	53(44)	54(56)	37(49)
LS%	74±5·5	72± 6	75± 6	41± 6
	(72±7)	(74± 5)	(76± 6)	(71± 6)
d-values of LS in water and process liquor	0·7	0·8	0·4	10
LR%	13±2	11± 2	10± 2	49± 8
	(11±2)	(12± 3)	(12± 3)	(20± 3)
dL%	1·5·	0·71	1·46	10·5
	Nil	Nil	Nil	5 to 8
	(—)	(—)	(—)	(—)
dD%	Nil	Nil	Nil	—130±12
	(—)	(—)	(—)	(—)
dS%	—110±20	—117±16	—100±25	— 20± 4
	(112±18)	(—118±16)	(—111±24)	(—118±16)

* Values in parenthesis indicate shrinkage values in respective process liquor.

Table 2

SHRINKAGE VALUES OF PICKLED COLLAGEN FIBRES UNDER VARIOUS EXPERIMENTAL CONDITION

Determination	Delimed samples	Pickled samples		
		in water 2-3 drops	in pickle medium	water, after placing the samples in plenty of water for 10 min.
T_s°C	53	36	48	52
LS%	74±5·5	42±5·2	78±7·2	69±8·0
LR%	11±2·0	47±8·0	7±2·5	10±1·5
dL%	Nil	4 to 7	—	Insignificant
(dD)%	Nil	—125±15	—	—166±25 first and nil after 10 minutes
(dS)%	—100±25	—20±4	—118±16.1	—156±30

in water is due to the absence of deliming effect of distilled water and hence better H-bond breaking ability of lime. Swelling forces of liming, it was reported,[3] bring about a change in the dimensional shrinkage properties of skin, particularly when samples tested in lime water; but the swelling forces are not sufficiently strong enough to bring about a change in the dimensional shrinkage properties of limed collagen fibres when tested in lime water. This is further proved by the insignificant or nil dL and dD values of limed collagen fibres on transferring the sample from lime water to water. Even the little swelling ability of lime water is decreased at the higher temperature because of a lowering in its solubility with temperature[5,6] and higher ionisation content of water[5,7] at higher temperature. Hence, influence of swelling which opposes the shrinkage in dimension is low at the shrinkage. Shrinkage properties of limed skin is influenced by the lime deposited within the pelt;[1,2,3] but there is less possibility of influence of deposited lime on shrinkage properties of limed collagen fibre bundles. Had there been any possibility of significant lime deposition, the LS values of limed samples would have been greatly reduced.

Lower T_s, LS and higher LR of pickled collagen samples in water compared to the value of those samples tested in pickle is again due to the influence of swelling forces caused by the limited dilution of pickle,[3] since only 2 to 3 drops of water is used as heating medium for carrying out micro shrinkage in water. Abnormally high dD value of pickled collagen fibre transferred to 2 to 3 drops of water for carrying out the shrinkage in water observed proves that the swelling of pickled collagen fibre in water is due to limited dilution of pickle. High dS value of pickled sample tested in pickle compared to those tested in water also substantiated this point. It should be noted in this connection that the dS values given in table 1 are not absolute since swelling of shrunken fibres is not always uniform. In the case of pickled skins, infinite dilution of pickle, in the short duration of heating of samples, is hindered by the three dimensional network of collagen structure though large amount of water is used as heating medium.

As a further proof that the limited dilution is responsible for the observed shrinkage behaviour of pickled fibres in water, adjacent pieces of one delimed and three pickled samples of about 0.2 cm. length were cut out. The pickled samples were respectively tested in a few drops of (a) water, (b) pickle and (c) water after transferring into large volume of water for 10 minutes to simulate the condition of infinite dilution. The delimed samples are tested in water. It is seen from Table 2 that pickled samples have an abnormally high dD value on transferring them into a few drops of water indicating swelling. This swelling subsides almost completely on transferring into a large volume of water and shrinkage values T_s, LS and LR) of these samples are comparable to those of delimed samples in water. This definitely confirms the influence of volume of water used as heating medium on shrinkage behaviour of pickled collagen fibre and also explains the insignificant difference in 'under tension' shrinkage values of delimed and pickled fibre samples reported[3] since in that case a large

volume of water is used as heating medium.

It is concluded that the use of process liquor instead of water lowers the T_s of limed collagen fibres and increases the T_s and LS values of pickled collagen fibres. LR value of pickled fibres are also decreased by the use of pickle. Swelling of pickled samples while testing in water is due to limited dilution of pickle.

Acknowledgment

This research has been financed in part by a grant made by the United States Department of Agriculture, Agricultural Research Service under PL 480.

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